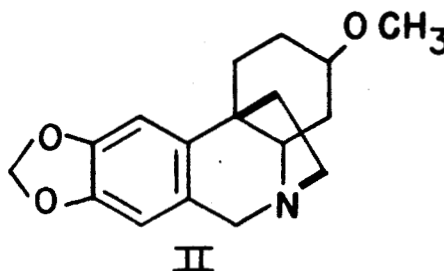
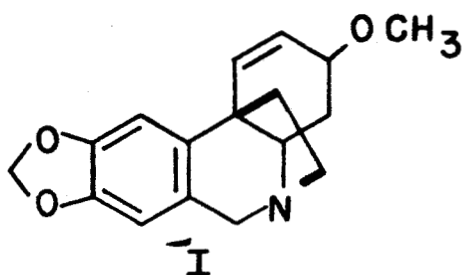


UNPUBLISHED PRELIMINARY DATA
INTERPRETATION OF THE HIGH RESOLUTION
MASS SPECTRUM OF DIHYDROBUPHANISINE^{1, 2}

Sir:

From low resolution mass spectral studies of the Amaryllidaceae alkaloids, buphanisine (I), dihydrobuphanisine (II) and their 7-methoxyl analogues, it has been noted that the fragmentation patterns of the 1,2-dihydro series are drastically different from those of the Δ^1 -unsaturated compounds^{3a, b}. In a previous communication⁴, structural correlations of the principle fragmentation pathways for buphanisine (I) were discussed in terms of mechanistic interpretations based on the unexpected



heteroatomic distributions which were observed in the spectrogram matrix tabulation.

We wish to report further results of considerable interest for their implications regarding the feasibility of the intercomparison of high resolution mass spectral data for molecules having closely related structural features. Such a comparison of the matrix tabulation (Table 1)⁵ for dihydrobuphanisine (II) with that for buphanisine (I)⁴ reveals striking differences among the column populations of heteroatomic contents C/HO₂, C/HO₃ and C/HNO₂. Thus, it is apparent

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CR-60468

(THRU)
None
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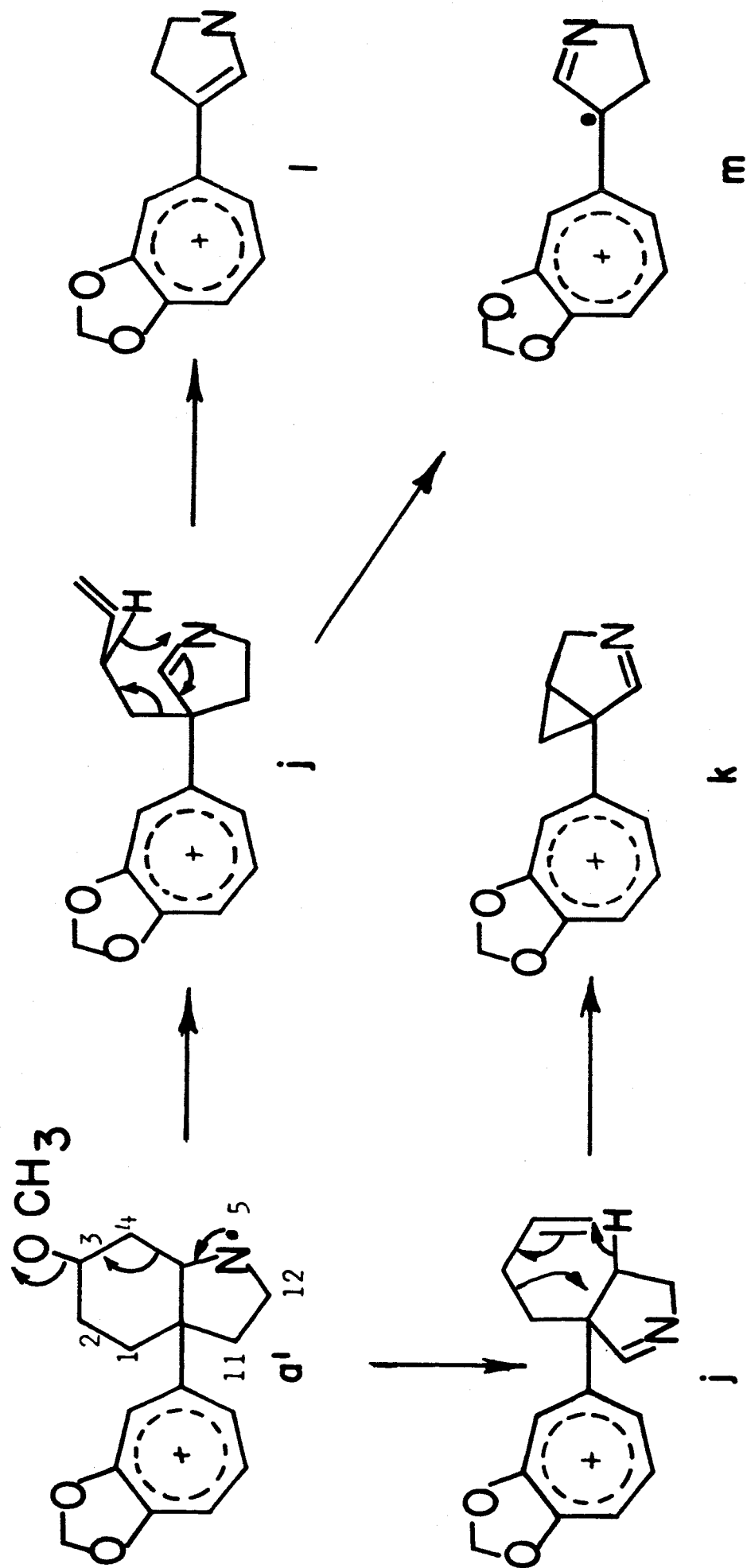
that this fragment array supports the conclusion that the principle modes of fragmentation for the carbon skeleton have been fundamentally changed by reduction of the 1,2-double bond.

This accurate mass data (Table 1) has revealed two major heteroatomic groups of ions: (2) since the retro-Diels-Alder elimination of azabutadiene⁴ is prevented in this saturated derivative, much of the total ion current is carried by fragments now containing the alicyclic nitrogen; and (b) the remaining ion current is borne by fragments having lost both the alicyclic nitrogen and the 3-methoxyl function. In Scheme 1, peaks containing the nitrogen have been depicted as arising via pathways starting with the "open" form of the molecular ion, a', in a fashion analogous to that proposed for the unsaturated alkaloid I⁶.

Thus it is most plausible that the ready loss of methoxyl radical may result from the assistance of the nitrogen radical (or lone electron pair) in the open form of the molecular ion a', producing ion j. Subsequent fragmentation by many pathways is available to the species j: (1) loss of neutral propene resulting in ion k ($C_{13}H_{12}NO_2$; analogous to M-71 in I); (2) loss of the neutral butadiene moiety by hydrogen rearrangement rendering ion l; and (3) simple cleavage of the 1,10b-bond with loss of butenyl radical yielding ion m (analogous to M-84 in I).

Consideration of the heavy population in the C/HO_2 heteroatomic grouping allows one to deduce that the lowest mass fragment in this series corresponds to the methylenedioxytropilium ion ($C_8H_7O_2$), probably arising from simple cleavage of the 10b,10c-bond in species a'. Since in species a' the C-10b carbon is quaternary and alpha to the charge-bearing tropilium moiety, it would not be expected that a fragment could be formed from the tropilium moiety plus one carbon atom,

SCHEME I



because three bonds would have to be broken. It is reasonable then, that the next fragments in this series correspond to two additional carbon atoms with attendant hydrogens ($C_{10}H_{7-9}O_2$), being C-10b and either C-1 or C-11. It should be noted that the highest mass fragment ($C_{15}H_{14}O_2$) in this heteroatomic grouping, must be formed from the molecular ion by loss of the nitrogen plus one carbon atom (methyleneimine⁷) in addition to the elements of methanol.

The structural correlations postulated in this communication are further substantiated by high resolution mass spectral data for other dihydroderivatives in the crinine series of Amaryllidaceae alkaloids which will be reported in a full paper in this series⁸.

A rather detailed understanding of the various modes of fragmentation operative in this series of alkaloids and their dependence on one structural feature has been deduced from two high resolution mass spectra, an analysis which was not possible from a systematic study of the conventional mass spectra^{3a, b}. From these results, it is clear that caution must be exercised in the interpretation of the significance of the heteroatomic distributions obtained from high resolution mass spectrograms. It has been shown that the matrix tabulation of two compounds of the same basal carbon skeleton display very different features.

Acknowledgements

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6. The possible representation of the open form, a', as a benzyl derivative cannot be excluded, but representation as a methylenedioxytropilium ion is consistent with the subsequent loss of formaldehyde to give substituted tropolone ions (CHO columns) and the subsequent loss of carbon monoxide from tropolone ions to give substituted benzene ions. The processes have been postulated as being operative in the methylenedioxybenzyl systems which can form the methylenedioxytropilium ion on electron impact (B. Willhalm, A. F. Thomas and F. Gautschi, Tetrahedron, 20, 1185 (1964); K. Biemann, Mass Spectrometry, McGraw-Hill Book Co., New York, 1962, p. 308). The loss of formaldehyde during tropilium ion formation has been confirmed by appearance potential measurements (J. M. S. Tait, T. W. Shannon and A. G. Harrison, J. Am. Chem. Soc., 84, 4 (1962)).
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